# PHYSICO-CHEMICAL CHARACTERIZATION OF PCBs

## FIZIČKO-HEMIJSKA KARAKTERIZACIJA ŠTAMPANIH PLOČA

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*Apstrakt*

*Reciklaža štampanih ploča (PCBs) je izuzetno složen i osetljiv postupak. Fizičko-hemijska karakterizacija štampanih ploča je od velikog značaja zbog izbora optimalnog postupka za preradu. Cilj ovog istraživanja bila je fizičko-hemijska karakterizacija ploča kao i izdvojenih frakcija nakon sečenja na šrederu i magnetne separacije. Izdvojene frakcije (metalni granulat, magnetna frakcija i plastika) su rastvarane u tri uzastopne faze, luženjem, uz korišćenje: sumporne kiseline, azotne kiseline i carske vode. Eksperimenti su izvedeni na frakcijama dobijenim preradom 100 kg uzorka i upoređivani su sa rezultatima dobijenim hemijskom analizom uzorka dobijenog ručnim rasklapanjem 10 ploča. Takođe, određivan je granulo sastav svake izdvojene frakcije.*

***Ključne reči:*** *PCB; reciklaža; granulometrijski sastav; frakcije*

*Abstract*

*Recycling of printed circuit boards (PCBs) is an extremely complex and sensitive process. Physico-chemical characterization of printed circuit boards is significant for choosing the optimal processing procedure. The aim of this research was the physico-chemical characterization of the boards and the separated fractions after cutting on a shredder and magnetic separation. Separated fractions (metal granulate, magnetic fraction, and plastic) were leached in three consecutive phases by use of sulfuric acid, nitric acid, and aqua regia. The experiments were performed on the fractions obtained by processing 100 kg of the sample and were compared with the results obtained by the chemical analysis of the sample obtained by manually unfolding 10 PCBs. Also, the grain size analysis of each separated fraction was determined.*

***Key words:*** *PCB; recycling; granulometric composition; fractions*

## 1 Introduction

Printed circuit boards (PCBs) are an integral part of modern electronic devices but contain heavy metals, organic substances, and chemical residues, which are a severe threat to the environment and human health [1-2]. On the other hand, waste printed circuit boards have a high residual value due to the presence of metals (about 28 % of the total weight) whose content in PCBs is up to several times higher than their content in natural mineral resources [3-4]. Precisely for this reason, recycling printed circuit boards plays a crucial role in environmental protection and economic development. In practice, mechanical, chemical and thermal methods are used for recycling PCBs [5-9].

The most commonly used method for recycling is the following stages: crushing and grinding and physical separation using magnetic or electrostatic methods. These procedures usually produce three fractions: Metal granulate, magnetic fraction and plastic (non-metallic fraction). The non-metallic fraction can be used as a filler for the production of high-strength composites [10-11]. This method of application is cheap and environmentally friendly. However, it is also inefficient due to metal loss during separation. The application of hydrometallurgical and pyrometallurgical technologies is much more efficient and profitable. Their disadvantage is that they require relatively high temperature (>200 °C) or high pressure. Also, waste gases generated in pyrometallurgical processes, as well as the use of acids in hydrometallurgical processes, can lead to serious environmental problems. Precisely for these reasons, recycling printed circuit boards is still a big challenge [12-13]. Also, the main problem is determining the chemical composition of the printed circuit boards. The group of authors [14-15] investigated pyrometallurgical, hydrometallurgical and electrometallurgical processes for the processing of electronic waste. Also, the research results of the combination of these procedures are presented in numerous of their works [14-16].

## 2 Results and discussion

The experiments in this research were performed on the fractions obtained by processing 100 kg of the sample (samples were obtained by cutting on a shredder and separating fractions on a magnetic separator). They were compared with the results obtained by the chemical analysis of the sample obtained by manual disassembly of 10 PCBs. In Table 1, it is shown the chemical composition of the obtained fractions. Table 2 shows elements distribution by-products and Table 3 shows a comparative chemical analysis. Separated fractions (metal granulate, magnetic fraction and plastic) were dissolved in three successive stages by leaching in sulfuric acid, nitric acid and aqua regia. This sample dissolution procedure was aimed at determining the exact chemical composition of PCBs. Chemical characterization of the solutions was performed using the Agilent 7900 ICP-MS.

*Table 1. Chemical composition by fractions*

| **[%]** | **B** | **Ti** | **V** | **Cr** | **Mn** | **Fe** | **Co** |
|---|---|---|---|---|---|---|---|
| P | 0.265201 | 0.02519424 | 0.00544 | 0.0011755 | 0.000254 | 0.022266 | 0.00069 |
| MG | 0.028448 | 0.041543 | 0 | 0.2850725 | 0.215046 | 16.20441 | 0.002194 |
| MF | 0 | 0.13031 | 0.00765 | 1.626447 | 0.224851 | 47.49278 | 0.050348 |
| **[%]** | **Ni** | **Cu** | **Zn** | **Sr** | **Mo** | **Ag** | **Cd** |
| P | 0.029396 | 19.019 | 0.372401 | 0.011704 | 2.58E-08 | 5.57E-09 | 0.000226 |
| MG | 0.362912 | 54.20531 | 9.4071 | 0.005577 | 0.00224 | 0.037481 | 0.000136 |
| MF | 2.593042 | 4.579222 | 4.9804 | 0.00895 | 0.016453 | 0.029026 | 0 |
| **[%]** | **Sn** | **Sb** | **Ba** | **La** | **Ce** | **Pr** | **Nd** |
| P | 0.007315 | 0.042427 | 0.021812 | 0.000293 | 0.000545 | 0 | 0 |
| MG | 8.664975 | 0.035728 | 0.016234 | 0.000146 | 0.000123 | 0.000258 | 0.004647 |
| MF | 1.183167 | 0.002279 | 0.322046 | 0 | 0 | 0 | 0.000212 |
| **[%]** | **Sm** | **Gd** | **Dy** | **Ho** | **Au** | **Pb** | **Bi** |
| P | 0 | 0 | 0 | 0 | 0.000346 | 0.076741 | 0 |
| MG | 0.000426 | 0.000202 | 0 | 0 | 0.017539 | 5.17939 | 0.035389 |
| MF | 0.00023 | 0 | 0.001251 | 0.001168 | 0.001233 | 0.37872 | 0.001472 |

**Not identified:** Li, Be, Sc, Ga, Ge, As, Se, Rb, Y, Zr, Nb, Ru, Pd, In, Te, Cs, Tb, Er, Tm, Yb, Lu, Hf, Ta, W, Ir, Pt, Ti, Th, U

*Table 2. Elements distribution by products*

| [%] | B | Ti | V | Cr | Mn | Fe | Co |
|---|---|---|---|---|---|---|---|
| P | 96.71 | 34.26 | 72.49 | 0.22 | 0.20 | 0.12 | 4.61 |
| MG | 3.29 | 17.93 | 0.00 | 17.06 | 52.84 | 28.61 | 4.65 |
| MF | 0.00 | 47.81 | 27.51 | 82.72 | 46.96 | 71.27 | 90.74 |
| **[%]** | **Ni** | **Cu** | **Zn** | **Sr** | **Mo** | **Ag** | **Cd** |
| P | 3.48 | 50.77 | 7.92 | 73.66 | 0.00 | 0.00 | 83.96 |
| MG | 13.65 | 45.93 | 63.50 | 11.14 | 13.81 | 60.30 | 16.04 |
| MF | 82.87 | 3.30 | 28.58 | 15.20 | 86.19 | 39.70 | 0.00 |
| **[%]** | **Sn** | **Sb** | **Ba** | **La** | **Ce** | **Pr** | **Nd** |
| P | 0.24 | 78.01 | 19.16 | 86.34 | 93.31 | 0.00 | 0.00 |
| MG | 89.39 | 20.86 | 4.53 | 13.66 | 6.69 | 100.00 | 96.27 |
| MF | 10.37 | 1.13 | 76.32 | 0.00 | 0.00 | 0.00 | 3.73 |
| **[%]** | **Sm** | **Gd** | **Dy** | **Ho** | **Au** | **Pb** | **Bi** |
| P | 0.00 | 0.00 | 0.00 | 0.00 | 5.54 | 4.21 | 0.00 |
| MG | 68.54 | 100.00 | 0.00 | 0.00 | 89.13 | 90.19 | 96.59 |
| MF | 31.46 | 0.00 | 100.00 | 100.00 | 5.33 | 5.61 | 3.41 |

*Table 3. Comparative chemical analysis*

| Element | Manual dissembled of PCB [%] | Mechanical dissembled PCB [%] |
|---|---|---|
| Ag | 0.00437 | 0.01243 |
| Cu | 18.6789 | 23.6015 |
| Sn | 5.23132 | 1.50549 |
| Pb | 0.82276 | 0.88964 |
| Ni | 0.49407 | 0.53192 |
| Au | 0.00128 | 0.00306 |
| Mn | 0.0026 | 0.08139 |
| Sb | 0.00748 | 0.03248 |
| Cr | 0.00055 | 0.33425 |
| Ba | 0.00037 | 0.07092 |
| Si | 0.00679 | |
| Mo | 0.00012 | 0.00325 |
| Zr | 0.00097 | |
| Sr | | 0.01001 |
| Co | 0.00018 | 0.00943 |
| Al | 0.26023 | |
| Mg | 0.00831 | |
| Cd | 0.00012 | 0.00016 |

| Element | Manual dissembled of PCB [%] | Mechanical dissembled PCB [%] |
|---|---|---|
| Bi | 0 | 0 |
| As | 0.00035 | 0 |
| V | 0 | 0.00473 |
| Ti | 9.35E-05 | 0.04633 |
| Se | 0.00029 | |
| Fe | 4.86707 | 11.3287 |
| Zn | 7.68756 | 2.9627 |
| Ca | 0.05677 | 0 |
| B | | 0.17277 |
| La | | 0.00036 |
| Ce | | 0.00036 |
| Pr | | 3.86E-05 |
| Nd | | 0.00073 |
| Sm | | 0.0001 |
| Gd | | 3.02E-05 |
| Dy | | 0.00021 |
| Ho | | 0.0002 |
| Bi | | 0.00556 |
| Insoluble residue | 61.88 | 59.61 |
| Σ | **100.013** | **99.4087** |

Figure 1 shows the technological scheme of sample dissolution. Particle size analysis of the obtained fractions is shown in Table 4; particle size distribution is shown in Figure 2. Grain Size analysis was determined on the Impact test sieve on the device Retsch Vibratory Sieve Shaker AS 200 using six sieves.

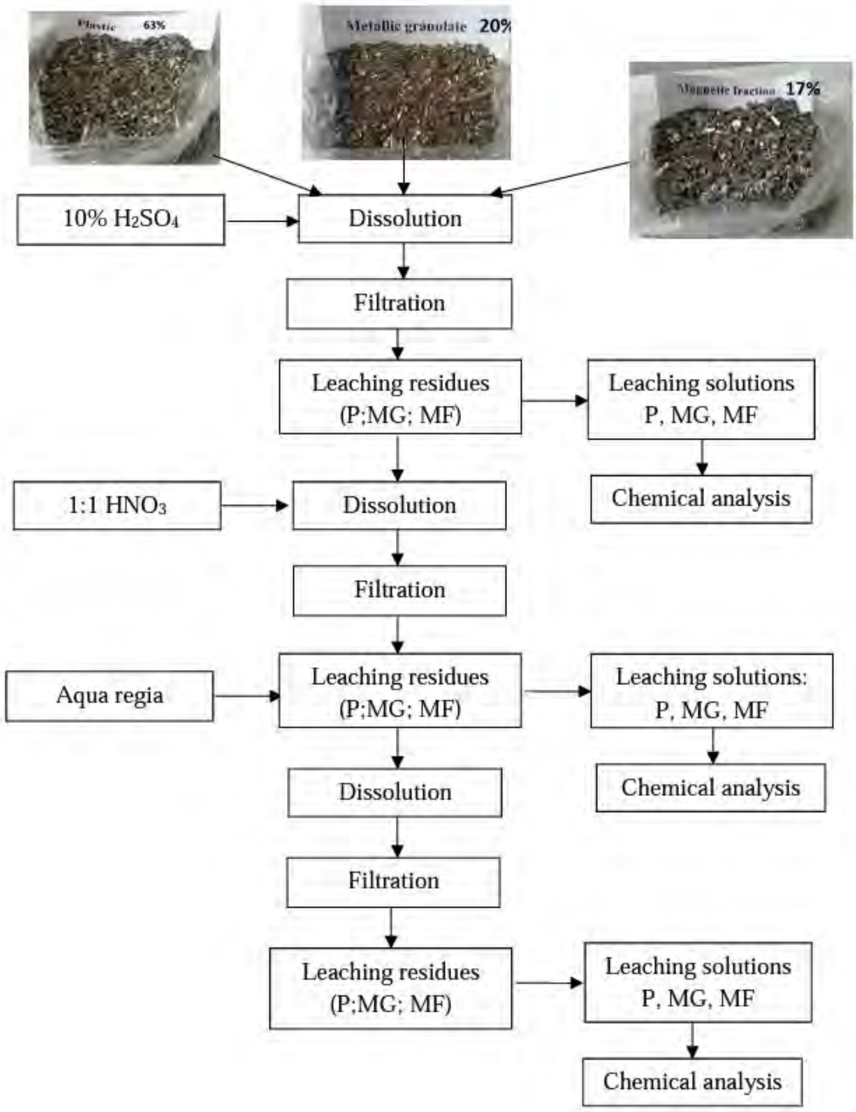


*Figure 1. Technological scheme of dissolving samples for chemical analyses*

*Table 4. Particle Size Analyses*

| Sieve size, mm | Plastic | | | Magnetic Fraction | | | Metallic Granulate | | |
|---|---|---|---|---|---|---|---|---|---|
| | m % | Pass. % | Ret. % | m % | Pass. % | Ret. % | m % | Pass. % | Ret. % |
| -16+8 | | | | 3.00 | 100.00 | 3.00 | | | |
| -8+4 | 16.95 | 100.00 | 16.95 | 49.75 | 97.00 | 52.75 | 8.15 | 100.00 | 8.15 |
| -4+2 | 51.20 | 83.05 | 68.15 | 28.70 | 47.25 | 81.45 | 42.15 | 91.85 | 50.30 |
| -2+1 | 24.05 | 31.85 | 92.20 | 11.50 | 18.55 | 92.95 | 34.35 | 49.70 | 84.65 |
| -1+0.5 | 6.75 | 7.80 | 98.95 | 5.40 | 7.05 | 98.35 | 14.65 | 15.35 | 99.30 |
| -0.5 | 1.05 | 1.05 | 100.00 | 1.65 | 1.65 | 100.00 | 0.70 | 0.70 | 100.00 |

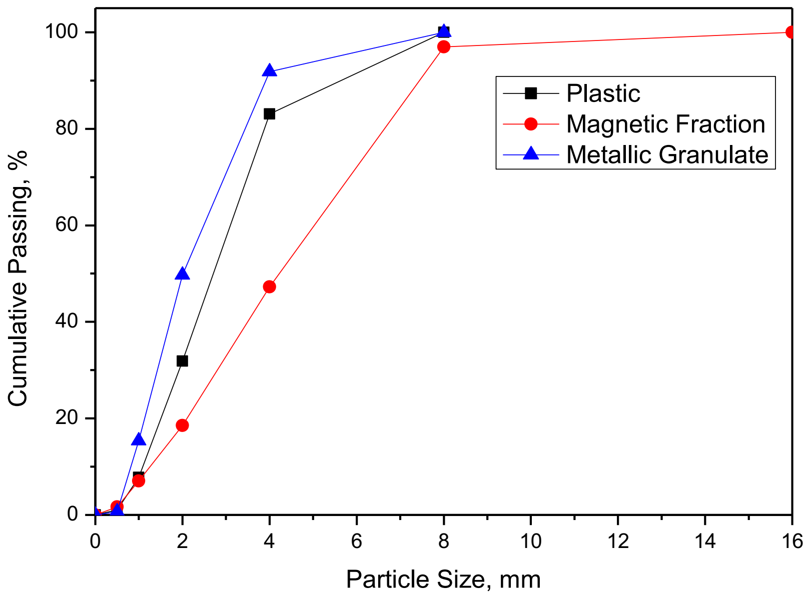


*Figure 2. Particle Size Distribution*

In order to determine the most accurate composition of the separated fractions after magnetic separation, dissolution was performed in three successive phases: sulfuric acid, nitric acid and aqua regia. In the first stage of dissolution, lead and part of the copper are eliminated in 10% sulfuric acid, while the dissolution in nitric acid (1:1) aims to dissolve primarily copper and silver. This phase is significant because of the dissolution of silver, which can then be precipitated with sodium chloride in the form of silver chloride, from which silver powder is obtained by dissolving in ammonia and precipitation with hydrazine. Also, removing the silver before dissolving it in aqua regia is very important. If the silver is not dissolved before this stage, a film of silver chloride is formed, which hinders further dissolution of the silver. Gold dissolves in aqua regia, which can be precipitated with sulfur dioxide, sodium nitrite or ascorbic acid.

The results showed that most of the copper, zinc, tin and lead are in the metal granulate, while iron and nickel are primarily distributed in the magnetic fraction. These are also the most abundant metals in PCBs, as shown in Tables 1 and 3. Due to further processing, it is necessary to reduce the tin and lead content in the metal granulate; that is, it is required to improve the process of separating the fractions after grinding (cutting on a shredder). Other tests should focus on researching the fractions obtained after separation on electrostatic separators.

The main goal of the research in this paper, which was to determine the optimal method of dissolving PCBs, i.e. determining their exact chemical composition, showed that pretreatment methods have a significant influence on the results of chemical analyses. In this paper, a comparative analysis of manually discarded printed circuit boards and boards was done after cutting on a shredder and separation by magnetic separation. Comparative chemical analysis of manually unfolded plates and products of magnetic separation (Table 3) showed a significant deviation in the content of tin (5.23% in manual preparation and 1.51% in machine preparation), chromium (two orders of magnitude), iron (4.87% for manual preparation, i.e. 11.32% for machine preparation) and zinc (7.69% for manual preparation, i.e. 2.96% for machine preparation). In comparison, the deviations in copper content are not large (18.68% for manual preparation, i.e. 23.60% for machine preparation). Of most significant importance for the further treatment of PCBs is the reduction of tin content, considering that tin is an element that has a negative impact on the process of electrolysis of anodes obtained by melting metal granules, as well as on the hydrometallurgical process of anode sludge processing.

## 3 Conclusion

The detailed chemical composition of the printed circuit boards according to the fractions obtained by magnetic separation (table 1) showed that the insoluble residue after dissolution is in three phases: plastic 80.10%, MG 5.25% and MF 36.37%, while the insoluble residue in compared to the original PCB samples is 61.88% for manually unfolded boards, i.e. 59.61% for boards processed on a shredder and magnetic separation. Research has shown that the method of preparation greatly influences the results of chemical analyses.


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